Interpreting Rainfall Changes as a result of the 8.2 ka Event through δ^2H ratios in the El Junco Lake, Galapagos

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Abstract

The most recent major climate perturbation, the “8.2 ka BP Event,” was a result of a mass influx of meltwater from the drainage of Lakes Agassiz and Ojibway into Hudson Bay. An influx of this magnitude has the potential to disrupt the Atlantic Meridional Ocean Circulation (AMOC) and likely also the behavior of the Inter Tropical Convergence Zone (ITCZ). Previous data indicated that the ITCZ shifted south in response to this event. The position of the ITCZ can be resolved from rainfall, which can be measured using the ratio of hydrogen isotopes (δ^2H). δ^2H was recorded in several molecular biomarkers collected from marine lake sediments in El Junco Lake, Galapagos Islands, which lies upon the southern edge of the ITCZ. These molecular biomarkers were Hexadecenoic Acid (Palmitic Acid, C16:0); Octacosanoic Acid (Montanic Acid, C28:0); dinosterol, a sterol produced by dinoflagellates, and C_{34} botryococcene, a sterol unique to *Botryococcus Braunii,* a form of green algae. δ^2H values increase around the time of the 8.2 ka event in dinosterol and botryococcene, which indicates a decrease in precipitation. The concentrations of botryococcene and dinosterol are characteristic of a period of drying. This implied decrease in precipitation, while not statistically significant does not coincide with previous data implying a southward shift of the ITCZ.

Plain Language Summary

The climate since the last ice age has been widely considered to have been predictably stable. However, meltwater from North American glacial sheets 8,200 years ago interrupted this climate, slowing the rate of the Atlantic Ocean’s overturning circulation, and causing a 200-year-long cold spell across Europe and North America. This would have altered the global system, including a band of rainfall along the equator that shifts positions because of atmospheric changes. The tropics play an important role in global climate, and to fully understand this, isotopic and molecular data was collected from marine sediments at El Junco Lake. Previous data shows that the intertropical convergence zone shifts south. However, isotopic and molecular data at El Junco Lake contradicts previous studies, showing that there are more complex dynamics at this location. Understanding how changes in the overturning circulation can be reflected in climate is especially important to understand in a rapidly changing global system.

Introduction

The tropical Pacific Ocean is a region that plays a vital role in regulating the global climate during interannual timescales via the El Nino/Southern Oscillation (ENSO) as well as on climate in decadal to orbital timescales. Regions as crucial to the global climate as the tropics can assist in understanding the impacts of abrupt climate changes on the global climate. The most recent of these climatic events occurred approximately 8.2 ka before the present day. This event caused broad-scale temperature drops in oceanic and terrestrial sites around the North Atlantic Ocean, suggesting a change in the thermohaline circulation (Alley et al 1997). Paleoclimate data suggests that this event was caused by the drainage of the glacial lakes Agassiz and Ojibway, releasing an estimated 163,000 km^3 of glacial meltwater into Hudson Bay (Barber et al 1999). A perturbation this large could sufficiently weaken the strength of the Atlantic Meridional Overturning Circulation (AMOC) due to the salinity anomaly that would result from the influx of fresh meltwater (Renssen et al. 2001, Lochte et al. 2019). Data reconstruction models illustrate the effects of the outburst flood being transmitted globally (Morrill et al., 2013, Matero et al., 2017). Ice cores showed a decrease in temperatures in the polar ice caps from $\delta^{18}O$ values in the Greenland highlands (Thomas et al 2007). Oxygen isotope records from Chinese cave stalagmites that can characterize changes in both the monsoon and global climate indicated a weakening of monsoon in the Northern hemisphere. (Cheng et al., 2009).

To fully understand the scope of the 8.2 ka Event, it is vital to understand the behavior of the tropical Pacific, of which there is limited data collected. The tropical Pacific Ocean plays a crucial role in climate regulation. Continental records indicated a gross shift in precipitation patterns, though little is known about the response of rainfall over the ocean itself. Low-altitude trade wind convergence combined with atmospheric convection form a heavy band of precipitation known as the intertropical convergence zone (ITCZ). The position of the ITCZ shifts as a result of warming and cooling of the atmosphere. Using oxygen isotope techniques, it was found that a more southern ITCZ corresponded with colder temperatures in the Northern hemisphere (Koutavas et al., 2004). There is a dearth of published rainfall records from the tropical Pacific resolving the 8.2 ka Event, without which it is impossible to state with certainty that a sudden freshening of the Northern Atlantic under interglacial conditions would force a displacement of ITCZ.

Attempts at reconstructing this ITCZ movement have faced the issue that the feature is most clearly defined over the ocean as opposed to on land. The high concentration of solutes can dampen the freshening effect (Berger & Killingley 1982) and the slow sedimentation rate in the open ocean limits the amount of data that can be collected in the open ocean. Rainfall records from saline freshwater lakes in the Galapagos (1S, eastern tropical Pacific) could assist in addressing this data gap, as it resolves complications of tracking in the open ocean.

The ratio of deuterium to hydrogen (δ^2H) is one method of reconstructing rainfall. A lower (or more negative) δ^2H is observed when more rainfall has occurred in part because it is preferentially rained out and because as greater rainfall occurs, the heavy isotope is diluted (Dansgaard 1964). As more rainfall occurs, the precipitation becomes increasingly 2H depleted, a phenomenon coined the 'amount effect' (Kurita et al., 2009). The culmination of these two processes gives rise to increased δ^2H values in drier conditions and deplete δ^2H values in wetter conditions **(Figure 1)**.

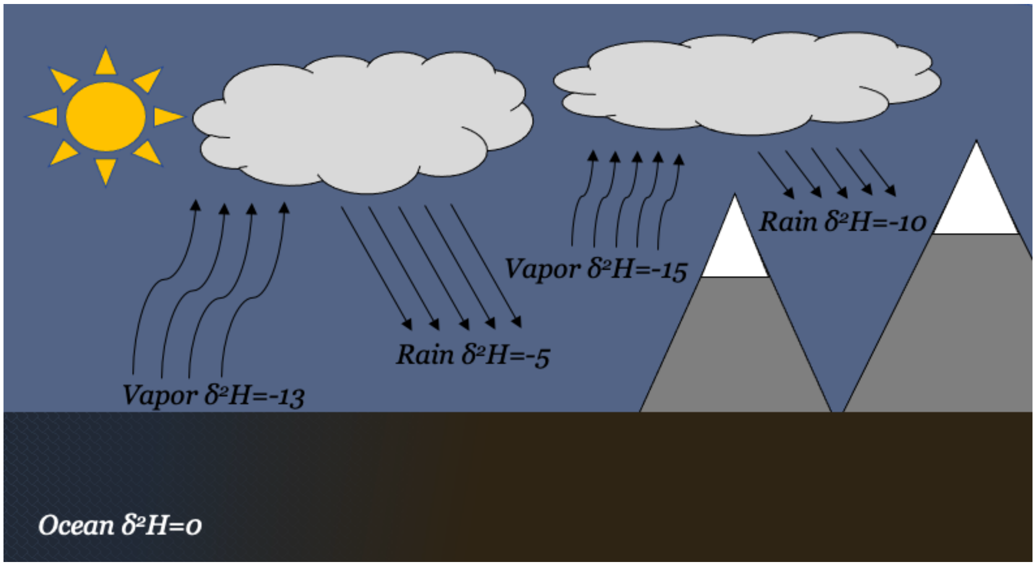

Figure 1. Diagram illustrating fractionation of deuterium isotope and selection of lighter isotope (1H) preferentially in vapor, and heavier isotope (2H) preferentially in rainfall.

The annual migration of the ITCZ seasonally as well as the resulting eastern Pacific El Nino events determine the amount of precipitation (Atwood and Sachs 2014). A shift of the ITCZ southward would cause drying in the Northern hemisphere and increased precipitation in the Southern hemisphere. Sachs et al. 2018 found that hydrogen isotope ratios of the algal lipid dinosterol increased in sediment cores in Palau (located at 7°N) in the western equatorial Pacific Ocean, which implies a reduction in precipitation.

The position of the ITCZ can be inferred using hydrogen isotope ratios taken from lipid biomarkers. The usage of a biomarker is vital to isolating that the factor influencing the isotopic changes is rainfall, and thus isolates changes in δ^2H. Variation was inferred from hydrogen isotope variations which are reliable hydroclimate proxies in Galapagos and Palau lake sediments (Atwood and Sachs, 2014; Nelson and Sachs, 2016; Sachs et al., 2018; Zhang et al., 2014). C16:0 is one of the most common saturated fatty acids and is abundant in both land and aquatic ecosystems. For this reason, it could serve as an important biomarker to enable conclusions on how hydrogen isotopes may have changed in response to the 8.2 ka Event. Both land and aquatic plants contain C16:0, but it is important to note that land plants are likely to be isotopically enriched in ^2H due to selective loss of the lighter hydrogen isotope through transpiration (McInerney et al. 2011). The land and aquatic plants can also be differentiated through the presence of octacosanoic acid (C28:0) which is not produced in aquatic ecosystems. The ratios of these can also assist in illustrating how large of a contribution is made by land plants, which would drive the δ^2H to be more positive. (Atwood & Sachs 2014) utilized the sedimentary ratio of two compounds (one produced by shoreline ferns and one produced by aquatic algae) to generate a hydrological record of sea level. In this case, larger C28:0: C16:0 would be indicative of a greater contribution of higher-order terrestrial plants, which may be a result of greater rates of erosion, which may be caused by factors such as changing wind or increased rainfall. Additional proxies include dinosterol, a sterol produced by dinoflagellates; and C_{34} botryococcene, a hydrocarbon unique to *Botryococcus Braunii,* a form of green algae. The concentrations of these compounds can be useful in reconstructing rainfall (Atwood & Sachs 2014).

El Junco Lake, located on San Cristobal Island, Galapagos lies in the eastern equatorial Pacific cold tongue (1°S and 87°E), and could be useful in understanding the behavior of the southern edge of the ITCZ in response to this precipitation **(Figure 2)**.

Figure 2. El Junco Lake (From Google Maps). It has a diameter of 270m and a maximum water depth of 6m. Its only inflow of water is from rainfall. Located along the band of heavy precipitation along the equator called the Intertropical Convergence Zone (ITCZ)

The use of hydrogen isotope and molecular records from El Junco Lake can resolve the position of the ITCZ through rainfall reconstructions as a result of a broad-scale cooling event resulting in a change of the Atlantic Meridional Ocean Circulation. Reconstruction of rainfall using sediment cores was collected to assist in providing a larger record of hydroclimate data. There was an emphasis on replication, using 2 cores to understand changes in δ^2H at El Junco Lake. An age model was created using ^{14}C dating and assisted in inferring how precipitation patterns have changed during and around the 8.2 ka Event at El Junco Lake. Due to the weakening of northern monsoons and drying at the northern edge of the ITCZ and modeling of a southern shift of the ITCZ when a cooler climate persists in the northern hemisphere, it was hypothesized that the ITCZ would shift southward, and this would be reflected in a decrease in δ^2H at El Junco Lake in all of the biomarkers.

Method

Sediment Collection

Two cores (EJ7 and EJ3) were collected from El Junco Lake in the Galapagos Islands in approximately 1m subsections in 2004. EJ3 had a transition from high to low-density sediment approximately 375 cm while EJ7 had this transition at approximately 450 cm depth, which is indicative of the Glacial-Holocene transition. These cores were sealed in the field and refrigerated at 4°C until core-splitting and subsampling in 1 cm sections occurred.

14C dating and chronology

A chronology for El Junco Lake was constructed from radiocarbon dates on sedimentary humin, which were treated with an acid-base-acid procedure according to the procedure outlined in (Brock et al., 2010) to remove extraneous organic materials, then sent to DirectAMS in Bothell, WA, USA for 14C dating by accelerator mass spectrometry. A calibration curve was created **(Figure 3).**

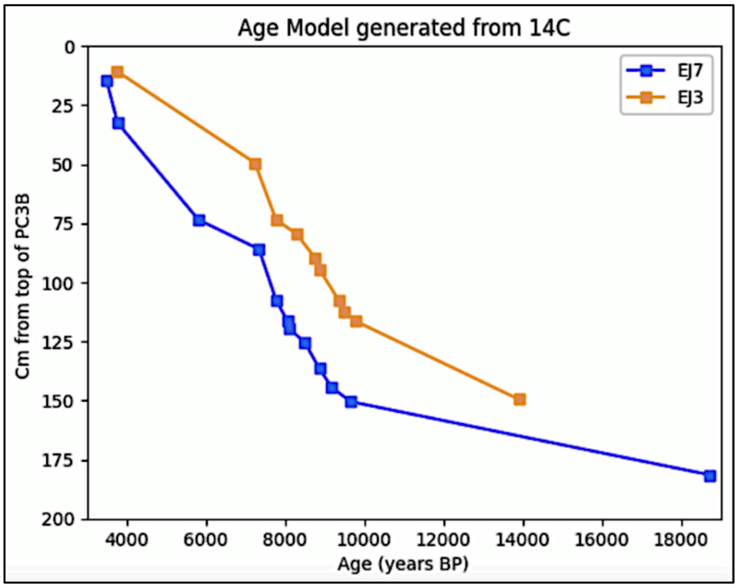

Figure 3. Age-depth relationship for cores EJ7 and EJ3. Ages derived from ^{14}C measurements based on radiocarbon dates from sediment subsamples.

Sediment Purification

Lipids were quantified and purified following the procedure detailed in (Nelson & Sachs, 2013; Nelson & Sachs,2014, Nelson & Sachs, 2016), 1 cm sediment subsamples were removed from cores and subsequently frozen and freeze-dried in combusted glass vials. Lipids were extracted from a known dry weight of sediment using 9:1 dichloromethane (DCM): methanol on an accelerated solvent extractor (ASE 200; Dionex Corp., Sunnyvale, CA, USA). Lipid extracts were then saponified using 10 mL 1M Potassium Hydroxide (KOH) in methanol and 3 mL HPLC grade water overnight at 70C. Saponified extracts were then acidified using 6M Hydrochloric Acid and then extracted from the water/methanol phase using hexane. Hexane extracts were then washed with water and dried using sodium sulfate columns. 1% aliquots of the lipid extracts were preliminary analyzed using gas chromatography flame-ionization detection (GC-FID). Lipid extracts were separated into fractions of different polarity by sequential elution from the aminopropyl gel (500mg) with the following solvents: 8mL 3:1 dichloromethane: isopropanol (NF1: neutral lipids), 8mL 4% acetic acid in ether, (NF2: acids) and 6 mL methanol (NF3: polar material). NF1 fractions were then acetylated at 70°C for 30 minutes in a mixture of 80uL pyridine and acetic anhydride, and then taken up in 20 µL DCM and 10 µL acetone. The acetic anhydride had a known isotopic composition with a δ^2H value relative to Vienna Standard Mean Ocean Water (VSMOW) of -132.9 +/- 6.6 permil. Sterol acetates were isolated using C18 reverse-phase high-performance liquid chromatography (HPLC). Dinosterol acetate and botryococcene acetate were identified via gas chromatography-mass spectrometry (GC-MS). The samples were then run using Isotope-Ratio Mass Spectrometry (IRMS), which were later corrected for derivatization. NF2 fractions were treated with 2mL hydrochloric acid made with 5mL acetyl chloride added to 50mL of dry methanol and methylated overnight at 70C to replace hydrogen in the carboxylic acid with a methyl group. The 2 batches of methylating reagent used had a δ^2H value relative to VSMOW of -65.3 +/- permil and 19 +/- 3.6 permil. Upon cooling, we added 2mL hexane and 1mL water and performed a liquid extraction, using sodium sulfate to isolate the lipid extract which was tested for correct derivatization using 5% aliquots and analyzed using GC-FID. The samples were then run using Isotope-Ratio Mass Spectrometry (IRMS), which were later isotopically corrected for the hydrogen added during derivatization. NF3 fractions were archived for future analysis.

Hydrogen Isotope Measurements

Isotope measurements are given as δ^2H values relative to VSMOW. Values calculated were corrected using a combined external isotope standard. Hydrogen isotope measurements were graphed using Python version 3.10.11 and compared to existing isotope measurements from other locations to generate a pattern of response to the 8.2 ka Event to understand ITCZ behavior.

Results

Sediment Chronology and Accumulation Rates

The age model produced from ^{14}C data markers (Figure 3) and interpolation would indicate a linear trend assuming that the sedimentation rate was constant as well as compaction. There was a larger accumulation of sediment over time between 8000 and 10000 years. With a higher resolution of data markers around the 8.2 ka Event, this range will have higher accuracy than depths over 10000 years ago, especially since the rate of accumulation had slowed based on the generated curve.

Botryococcene concentrations and δ^2H values

C_{34} botryococcene is one of the more abundant lipids in marine sediment at El Junco Lake. These botryococcenes are produced by a single race of the green algae *B. braunii* (Zhang et al. 2007). Concentrations of C_{34} botryococcene ranged from 0-158.32 µg per g of extracted sediment in EJ3. In EJ7, concentrations were especially high at the top of PC3B, with values as high as 280.82 µg/g and values fell around the 8.2 ka Event **(Figure 4)**. In both cores, concentrations fell to a minimum during the period of the 8.2 ka Event, and increased substantially after 8000 years BP. The concentrations were highly variable.

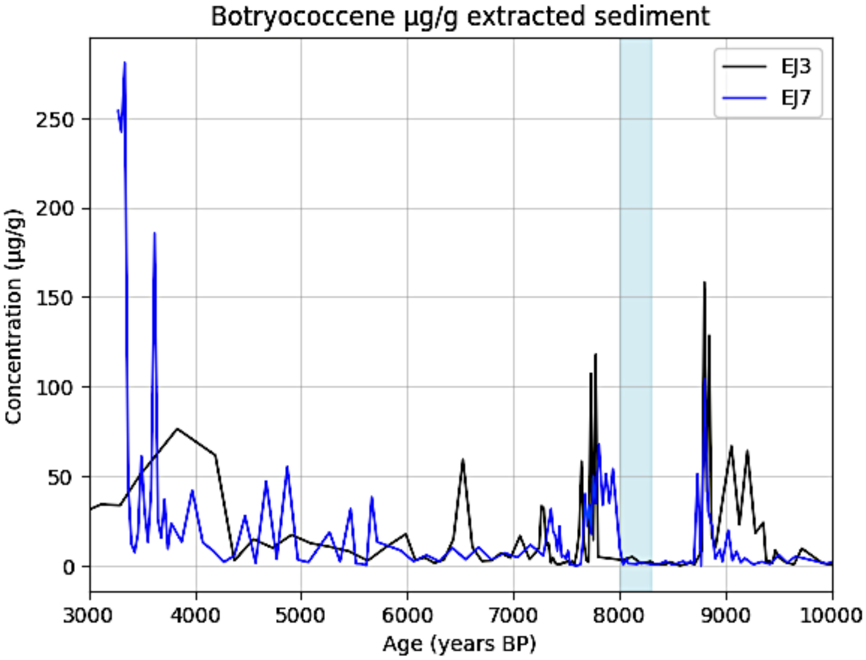

Figure 4. Lipid biomarker (C_{34} botryococcene) concentration in ug per g of extracted sediment. Highlighted date range indicates estimated duration of effects of 8.2 ka Event.

δ^2H values relative to VSMOW of botryococcene were collected and were in similar ranges for both EJ3 and EJ7 (Figure 5). In EJ3, botryococcene δ^2H values showed sharp decreases at 5090 and 7288 years BP. In EJ7, δ^2H values experienced similar ranges of variability, with sharp decreases at 3526, 6918, and 8670 years BP. After the 8.2 ka Event, δ^2H increased relative to the data points around it, whose deviations can primarily be tied to oscillations in El Nino.

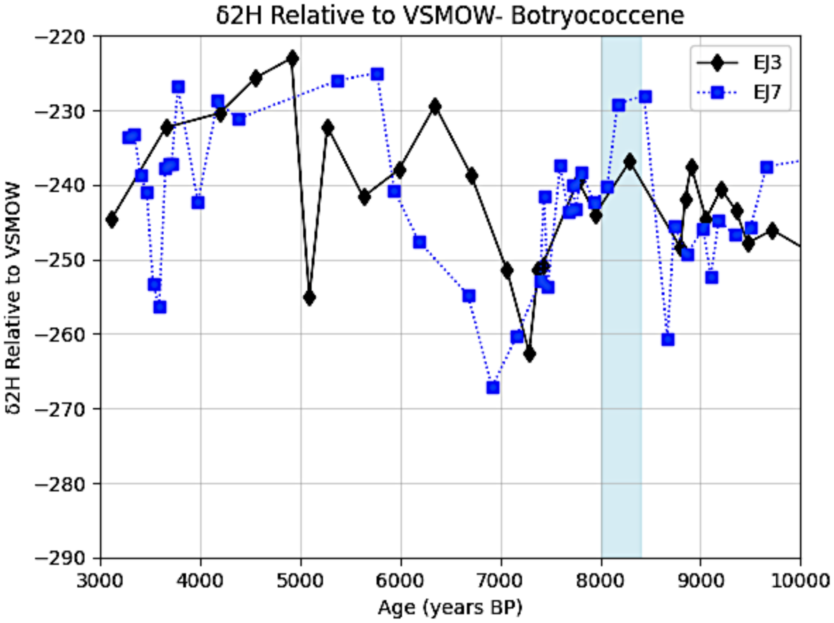

Figure 5. δ^2H record of C_{34} botryococcene. δ^2H values are relative to VSMOW. Highlighted date range indicates estimated duration of effects of 8.2 ka Event.

Dinosterol concentrations and δ^2H values

Dinosterol is also an important sterol, produced by dinoflagellates in El Junco Lake. Atwood et al. 2014 noted that the sterol composition indicated that the genus *Peridinium* had been the primary source of dinosterol in El Junco Lake throughout the sedimentary record. Concentrations of dinosterol were highly variable. **(Figure 6**) In EJ7, the concentration of dinosterol (range 0.00-44.06 µg per g of extracted sediment) was generally higher than that of EJ3 (range 0.00-10.74 µg/g). At the time of the 8.2 ka event, dinosterol concentration increases to 10 µg/g in both EJ3 and EJ7.

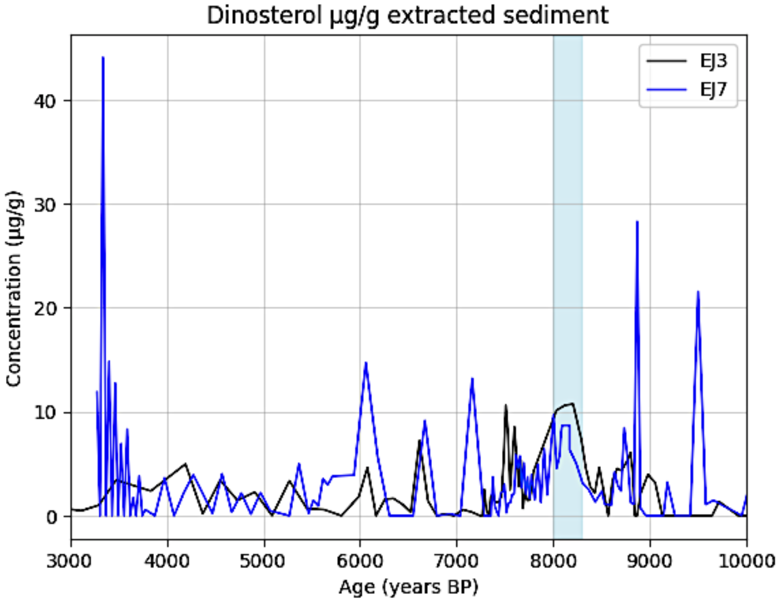

Figure 6. Lipid biomarker (dinosterol) concentration in ug per g of extracted sediment. Highlighted date range indicates estimated duration of effects of 8.2 ka Event.

The record of δ^{2}H values corresponding to the lipid biomarker dinosterol is less complete than the record corresponding to botryococcene due to the lower concentration throughout the core. In both EJ3 and EJ7, there is a significant in δ^{2}H values around the time of the 8.2 ka event **(Figure 7**).

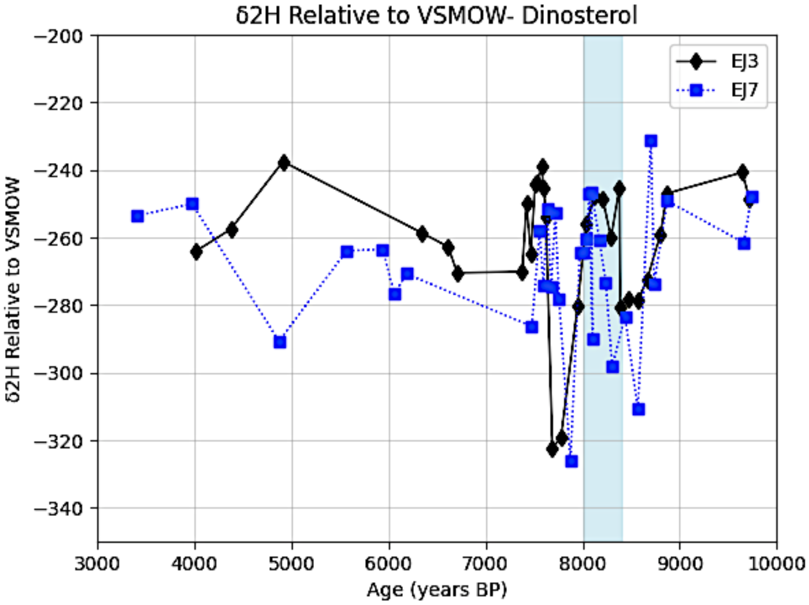

Figure 7. δ^{2}H record of dinosterol. δ^{2}H values are relative to VSMOW. Highlighted date range indicates estimated duration of effects of 8.2 ka event.

Fatty Acids δ^2H values

The 2H/1H ratio of C28:0 and C16:0 showed similar patterns, although overall, C28:0 was enriched in deuterium **(Figure 8)**. In the EJ7 core, there is a large quantity of data and a high degree of variation of 2H/1H around the 8.2 ka Event of interest for both the C16:0 and C28:0 data series, while in the EJ3 core, which has a longer time series, there only appears to be a very slight dip in as δ^2H values relative to VSMOW around the 8.2ka Event. After 10000 years, values continue to drop for C16:0 in both EJ7 and EJ3, while in the C28:0 series, it remains relatively constant.

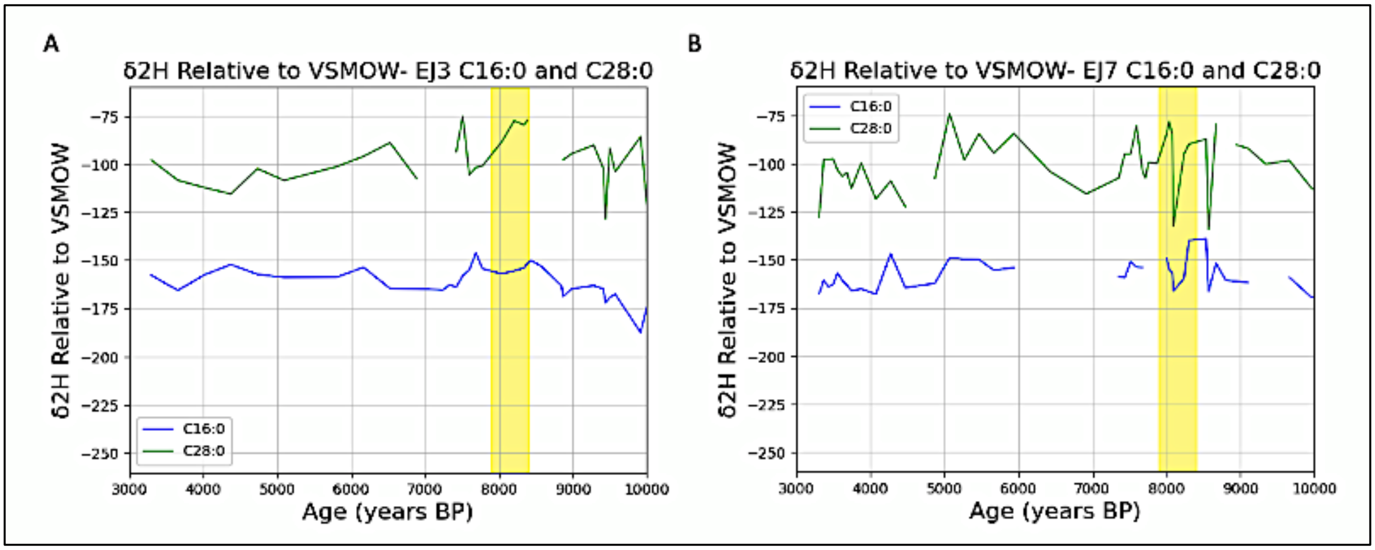

Figure 8. δ^2H values relative to VSMOW were plotted against ages constructed from the interpolated age model for the (A) EJ3 core for C16:0 and C28:0. (B) EJ7 core for C16:0 and C28:0. Highlighted date range indicates estimated duration of effects of 8.2 ka Event.

Ratio of C28:0: C16:0

Due to the differing isotopic compositions of hydrogen between C28:0 (produced by higher-order terrestrial plants) and C16:0 (present along terrestrial ecosystems and in aquatic systems as well), taking a ratio of the concentrations of the fatty acids assists in understanding the extent of terrestrial input. Variability was high, though in both cores the ratio between C28:0 and C16:0 was literally in the range of 0-3. Exceptionally high points were present in EJ3 (12.98 and 43.21). Around the time of the 8.2 ka Event, the ratio in EJ7 increased, while in EJ3 there was no discernible change **(Figure 9)**.

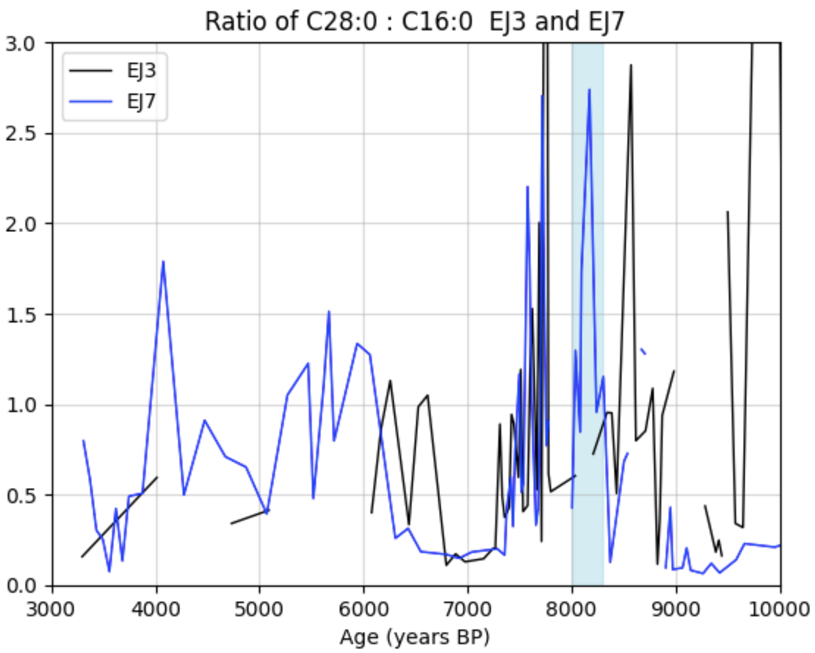

Figure 9. The ratio of C28:0: C16:0 concentrations per g of extracted sediment plotted against the age as interpolated from depth in the core. Highlighted date range indicates estimated duration of effects of 8.2 ka Event.

Discussion

Of the biomarkers used, there was a great degree of variability in δ^2H values across the 4 biomarkers (botryococcene, dinosterol, C16:0 and C28:0), indicating that it is difficult to draw a straightforward conclusion about whether rainfall changed appreciably as a result of the 8.2 ka Event.

C_{34} botryococcene is a sterol unique to *Botryococcus Braunii*. Its concentration throughout the core varied significantly, but around the 8.2 ka Event its concentration was very close to 0 **(Figure 4)**. The sterol, produced only by a single race of the green algae, has its concentration controlled by levels of oligotrophy, thriving in oligotrophic conditions while its abundance decreases with an increase in nutrients, including NH4 (Smittenberg 2005). The low concentration may be due to increased competition for nutrients which would thus result in a decrease in the population. The δ^2H values show an increase of 2H and less negative values corresponding to the 8.2 ka event **(Figure 5)**. Dinosterol concentrations (µg per g of extracted sediment) observed throughout EJ3 and EJ7 varied less than botryococcene **(Figure 6).** Dinosterol concentrations increased after the 8.2 ka Event. Dinoflagellates of this genus have been found to thrive in a variety of environmental conditions when compared to *B. Braunii*. The

δ^2H values show an increase of 2H and less negative values corresponding to the 8.2 ka Event **(Figure 7).**

The sedimentary biomarker concentrations of dinosterol and botryococcene at El Junco Lake support the theory that the organisms that produce the two lipid biomarkers bloom in different environmental conditions. The concentration profiles exhibit opposite trends, and the concentration of botryococcene was anti-correlated with its δ^2H, while dinosterol was positively correlated with its δ^2H, which is consistent with findings in Atwood & Sachs 2014. Conditions favorable for *B. Braunii* are associated with moderate to strong El Nino events, so the sharp decrease in concentration is indicative of a weakening of El Nino. There is a lack of resolution for dinosterol due to it having a low concentration in the core overall, though the increase in dinosterol concentration contributes to the idea that dinoflagellates and botryococcene occupy different ecological niches and are in competition for nutrients.

The fatty acid record is more complex. The δ^2H record shows significant deviations between the EJ3 and EJ7 cores **(Figure 8).** Due to transpiration, C28:0 and C16:0 have different δ2H values (McInerney et al. 2011). EJ3 shows a slight dip in both values, which would correspond to increased precipitation, but does not show an increase in terrestrial input. EJ7 shows a great degree of variation around the 8.2 ka Event in the δ^2H record as well as a significant increase in terrestrial input, as understood from the ratio of C28:0 to C16:0 **(Figure 9)**. Higher ratios of C28:0 may be indicative of increased input from terrestrial systems. There are very large ratios of C28:0: C16:0 indicative of a great degree of terrestrial plant residue in sediment but this could also be indicative of C16:0 loss. Increased terrestrial input may also be a result of increased erosion, which may be accelerated by dry conditions and changing winds, though this wouldn't explain the behavior of the δ^2H record which does not agree with the other biomarker records. This may be indicative of a more complex system at El Junco Lake than previously understood.

While the values do not demonstrate enough statistical significance to conclude a statistically significant change in precipitation as a result of the 8.2 ka Event, δ^2H values from botryococcene and dinosterol increase indicating a period of dryness. Changes in precipitation at this location were previously thought to only have been a result of ITCZ shifts, which previous records and models propose would shift southward due to the 8.2 ka Event. δ^{18}O values from Chinese cave stalagmites indicated a weakening of the northern monsoon (Cheng et al 2009). δ^{18}O records of biogenic carbonate from northwestern India also indicated a weakening of the India

Summer Monsoon (Dixit et al. 2014). A weakening of the northern monsoon indicates a shift to a more southern ITCZ, which may reflect the change in AMOC. Sachs et al 2018 found an increase in δ^2H values in analyses of the algal lipid dinosterol on the northern edge of the ITCZ from lake sediments in Palau, indicating a southward shift. El Junco Lake lies along the southern boundary of the ITCZ, and previous models would have predicted an increase in precipitation as a result, which was what was initially proposed in this study. However, the δ^2H record combined with changes in biomarker concentration consistent with a dry period contradicts previous research.

The mechanism of global climate is a phenomenon that is only beginning to be understood, particularly when considering the dynamics of rainfall and climate. Modeling of the AMOC is still in development and could better assist in understanding how shifts in AMOC strength affect the position of the ITCZ. The disparities between the EJ3 and EJ7 cores are statistically significant and make it unable to draw a conclusion with certainty, so another parallel core may be of assistance when combined with δ^2H, δ^{16}O, and other paleoclimate proxies.

Conclusion

Past changes in rainfall associated with the 8.2 ka Event, a well-studied and resolved occurrence that involved the outburst of glacial meltwater in the Labrador Sea in the North Atlantic Ocean, were reconstructed from marine sediments from El Junco Lake using both the concentration and the hydrogen isotope composition of four biomarkers (dinosterol, botryococcene, C28:0 and C16:0). Dinosterol is interpreted as a record for long term rainfall, while botryococcene is interpreted as a record for El Nino Events. C28:0 (produced by terrestrial plants) and C16:0 (produced by aquatic algae) $\delta\,^2$H and the sedimentary ratio of those two compounds provided an additional proxy. Botryococcene and dinosterol indicated that $\delta\,^2$H increased around the 8.2 ka Event, and terrestrial input increased. This indicates a decrease in precipitation, the most likely cause of which is a shift in the ITCZ northward. Though many models indicate that a southward shift of the ITCZ would occur given a sudden freshening of the North Atlantic Ocean and thus a weakening of the strength of the AMOC, there is not yet statistically significant data to indicate an equatorward shift at El Junco Lake. Preliminary observations show a northward migration which is inconsistent with previous data findings, though this may be due to El Junco having more complex climate dynamics than initially thought. Improved representation of maritime rainfall in tropical climates will assist in the general understanding of global climate, including responses to major climatic events.

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